

## Iron Nitride Catalysts For Synthesis Reactions

W.N. Delgass, A.A. Hummel, A.P. Wilson, and K.E. Hummel

School of Chemical Engineering  
Purdue University  
West Lafayette, Indiana 47907

### INTRODUCTION

Synthesis gas (CO and H<sub>2</sub>) from coal is a potential source of both fuels and chemical feedstocks. Commercial applications of this technology use iron-based catalysts, which are known to carburize during reaction (1-5). Pre-nitriding of a fused iron catalyst has been reported to shift the molecular weight and alcohol content of the product distribution (6,7). Recent studies (8,9) indicate somewhat different selectivities for the nitrified catalysts, but confirm high activities and stability of nitrogen for a variety of catalyst and reaction conditions.

The structures and magnetic properties of the nitride phases have been investigated by various authors using several techniques, including XRD (10), LEED (11), Auger (12) and Mössbauer spectroscopy (13,14,15). Three nitride phases have been differentiated:  $\gamma$ -Fe<sub>4</sub>N,  $\epsilon$ -Fe<sub>x</sub>N (2 < x < 3), and  $\zeta$ -Fe<sub>2</sub>N. The phase diagram has been presented by Ertl *et al* (12). As the nitrogen content increases, the structure changes from BCC ( $\alpha$ -Fe), to FCC ( $\gamma$ -Fe<sub>4</sub>N), to HCP ( $\epsilon$ -Fe<sub>x</sub>N), to orthorhombic ( $\zeta$ -Fe<sub>2</sub>N). Mössbauer spectroscopy is particularly effective in differentiating the various iron nitrides (14,15).

In this work, we have used Mössbauer spectroscopy and transient mass spectrometric analysis to examine the stability, surface chemistry, and catalytic behavior of the three iron nitrides. We have found that at typical reaction temperatures, the pure nitride phases are unstable in both H<sub>2</sub> and synthesis gas, but in synthesis gas much nitrogen can be retained in the working catalyst in a carbonitride phase. We have continued this work by examining the nature of the surface before and during reaction in synthesis gas. Transient measurements show that surface nitrogen species are more reactive toward hydrogen than surface carbon species, and thus nitrogen is quickly lost from the surface during the first minutes of reaction. The high reactivity of nitrogen also suggests that a continuous supply of nitrogen from a reactant could lead to synthesis of nitrogen-containing compounds. The patent literature and our preliminary experiments confirm production of acetonitrile when NH<sub>3</sub> is added to synthesis gas at 700 K. Our findings also indicate that the use of catalysts with very small iron particles can affect the stability during reaction.

### EXPERIMENTAL

Preparation of the unsupported nitride powders was accomplished by reducing iron oxide at 325-400 °C in flowing UHP hydrogen. The reduced iron powder (a compressed wafer in the Mössbauer apparatus, and a packed bed for the transient mass spec apparatus) was nitrified in a flowing mixture of ammonia and hydrogen for about 4 hours to produce the catalyst product. The nitrogen content was controlled by either altering the gas phase ammonia composition or varying the reaction temperature. Nitrogen content was checked by integrating the

mass spectrometer signal for  $\text{NH}_3$  when the nitride was reduced in hydrogen. Nitride phases were also identified by their Mössbauer spectra or XRD patterns.

The  $^{57}\text{Fe}$  Mössbauer spectra were recorded on a Nuclear Data multichannel analyzer from an Austin Science S-600 spectrometer. Both constant acceleration and constant velocity (transient) modes were used. All Mössbauer spectra isomer shift parameters are referenced to a  $25\mu\text{m}$  NBS Fe foil. The *in situ* Mössbauer cell supports a mechanically compressed sample wafer, allowing Mössbauer effect investigation of changes in the bulk sample during nitriding, denitriding, carburization, and synthesis reaction.

Details of reaction kinetics are studied by mass spectrometry. The apparatus used for this portion of the work was specifically designed for transient experiments. Combinations of reactant feed gases can be stepped or pulsed to the reactor. The effluent of the reactor is continuously measured by an Extranuclear EMBA II quadrupole mass spectrometer with a supersonic nozzle molecular beam inlet and phase sensitive detection. The spectrometer is controlled and monitored by a Digital MINC 11 microcomputer to facilitate the high speed gas analysis required for transient experiments.

## RESULTS AND DISCUSSION

The Mössbauer spectral variations with changing nitrogen content are depicted in Figure 1, with  $\alpha\text{-Fe}$  included for comparison. The  $\zeta\text{-Fe}_2\text{N}$  phase can be made at a variety of temperatures, but is most easily prepared at  $400^\circ\text{C}$  with 100% ammonia and identified by the narrowly split quadrupole doublet of Figure 1A. The  $\epsilon\text{-Fe}_x\text{N}$  phase is only prepared in a narrow concentration range of  $90 \pm 5\%$   $\text{NH}_3$ . Variation of the temperature changes the stoichiometry ( $2 < x < 3$ ) such that decreasing nitrogen content increases the species with hyperfine splitting of about 200kOe at the expense of the central quadrupole doublet (Spectra 1B-E). Slight changes in concentration also alter the stoichiometry of the  $\epsilon\text{-Fe}_x\text{N}$  phase (Figure 1F). The  $\gamma\text{-Fe}_4\text{N}$  phase is formed at lower ammonia concentrations (75%  $\text{NH}_3$ ) at  $325^\circ\text{C}$ , and is easily identified by its characteristic 8 line spectrum with its rightmost line at higher velocity than that of  $\alpha\text{-Fe}$  (Figure 1G).

The constant velocity capability of the Mössbauer drive allows *in situ* inspection of the nitriding process by following the growth or loss of transmitted intensity at a fixed velocity during the process. Figure 2 presents the loss (increase in transmission) and subsequent return of the central quadrupole doublet during denitriding and reinitriding of  $\zeta\text{-Fe}_2\text{N}$ , observable by following the velocity indicated in the constant acceleration spectrum. The denitriding kinetics at  $325^\circ\text{C}$  are very rapid, converting the  $\zeta$  nitride to  $\alpha$  iron in seconds. On the other hand, the nitriding to the orthorhombic phase is relatively slow. During nitriding the nitrogen entering the lattice promotes a structural change from the relatively open bcc structure to the more dense orthorhombic arrangement which has considerably lower diffusivity of nitrogen. Ninety percent of the nitrogen appears to have entered the sample within 40 minutes of starting the nitriding.

Figure 3 shows the effect of gas phase composition on the rate of orthorhombic phase disappearance from  $\zeta\text{-Fe}_2\text{N}$ , as followed by constant velocity measurement of the central doublet at 0.5 mm/sec in the Mössbauer spectrum. The effect of pure hydrogen at  $325^\circ\text{C}$  has already been seen in Figure 2. At  $250^\circ\text{C}$ , the nitrogen loss remains rapid (Figure 3A). Removal of nitrogen in the form of  $\text{N}_2$  in He is very much slower (Figure 3B). The phase disappearance is very fast in  $3\text{H}_2/\text{CO}$  as well, (Figure 3C) but in this case does not reflect fast loss of substantial nitride nitrogen to ammonia in the gas phase. Constant acceleration spectra taken

after 20 minutes of exposure to  $3\text{H}_2/\text{CO}$  show that the initial contact with syngas first removes nitrogen from the lattice to form an  $\epsilon$  nitride, which has small contribution at the 0.5 mm/s velocity. Further reaction in synthesis gas then produces carbonitrides. Carburation in pure CO produces only a gradual structural change (Figure 3D). The final phase, as confirmed by the constant acceleration spectrum, is a very broad doublet which has little definition (less even than the spectrum in Figure 1D).

Investigation of the mechanism of nitride decomposition in hydrogen can be studied by mass spectrometry. In addition, surface species present during the nitriding process in ammonia can be identified by decomposition in deuterium. Figure 4 shows the decomposition of a  $\zeta\text{-Fe}_2\text{N}$  in deuterium into the deuterio-ammonias at  $250^\circ\text{C}$ . The  $\zeta\text{-Fe}_2\text{N}$  nitride was prepared in  $\text{NH}_3$  at  $400^\circ\text{C}$ , then cooled to  $250^\circ\text{C}$  in  $\text{NH}_3$  and the reactor then purged with argon for 10 minutes. The nitride and surface species are stable in argon at  $250^\circ\text{C}$ . The decomposition in  $\text{D}_2$  occurs quickly, as predicted from the Mössbauer results in Figure 2. From the shape of the  $\text{ND}_3$  curve, which is the decomposition product of the nitride nitrogen, it is clear that a slow activation is taking place. Modelling of this phenomenon indicates that a surface competition between the amount of adsorbed hydrogen (or in the case of Figure 4, adsorbed deuterium) and a nitrogen surface species can successfully simulate the results. Bulk nitride is converted to this nitrogen surface species.

Also apparent in Figure 4 are the mixed ammonias with hydrogen contributions. The presence of  $\text{NH}_x\text{D}_{3-x}$  in the effluent shows clearly that the fresh surface retains some hydrogen. The appearance of  $\text{NH}_3$  first does not indicate that  $x = 3$ , but is the result of chromatographic isotopic exchange at the leading edge of the deuterium pulse. This hydrogen most probably exists as a stable  $\text{NH}_x$  surface species left over from the nitriding procedure in  $\text{NH}_3$ . It will be seen that this  $\text{NH}_x$  species is very reactive and is removed in synthesis gas.

The deuterium experiment and the Mössbauer studies show that some of the nitrogen in the pure nitrides is very labile. The transient mass spectrometric approach allows us to measure relative surface reactivities directly. Figure 5 shows the response of a freshly prepared and He-purged surface to  $3/1 \text{ H}_2/\text{CO}$ . The curves show clearly that surface hydrogen reacts preferentially with surface nitrogen rather than surface carbon. About 1.6 monolayer's worth of ammonia comes off before methane production starts. The  $\text{CO}_2$  curve shows that carbon is being deposited on the surface by the Boudouard reaction while hydrogen is being scavenged by the surface  $\text{NH}_x$  groups. The availability of surface species changes dramatically after five minutes on stream. Figure 6 shows the response of the reacting system to a short He pulse followed by a switch to hydrogen. The burst of methane is characteristic of excess surface carbon. Ammonia evolves only slowly from the catalyst. Because of the high reactivity of surface nitrogen species just demonstrated above, we take this result to indicate very low nitrogen content on the the surface of the working catalyst. The high reactivity of surface nitrogen with hydrogen can be delayed, but not suppressed, by the presence of excess surface carbon. If the surface of a fresh nitride is precarburized in CO and then exposed to synthesis gas, as shown in Figure 7, the surface carbon layer delays any activity for a short induction time, but then nitrogen is released as ammonia before carbon can react to methane. The surface  $\text{NH}_x$  species is therefore stable in helium or pure carbon monoxide at  $250^\circ\text{C}$ .

We have also begun studying iron nitrides supported on carbon. A small particle 5% iron on Carbolac-1, which is a high surface area ( $1000 \text{ m}^2/\text{g}$ ) carbon support, was prepared and reduced in hydrogen for 16 hours at  $400^\circ\text{C}$ . The room temperature Mössbauer spectrum of this reduced catalyst is shown in Figure 8a. The broad singlet at 0.0 mm/sec may be ascribed to superparamagnetic  $\text{Fe}^0$ . The typical six line pattern collapses to a superparamagnetic

singlet when the relaxation time is short compared to the lifetime of the excited state of the nucleus. We may therefore conclude that our iron crystallites are small. The asymmetric nature of this spectrum is due to the contribution of  $\text{Fe}^{2+}$  at 0.8 mm/sec, which arises from incomplete reduction of the passivated iron. Extensive (21 hrs) exposure to UHP He that was further purified in oxygen traps resulted in the spectrum of Figure 8b. The increased absorbance of the  $\text{Fe}^{2+}$  peak indicates that the catalyst is passivated in helium with oxygen concentrations on the order of 1 ppb. This catalyst was nitrified in pure  $\text{NH}_3$  at  $400^\circ\text{C}$  for 8 hours to produce the  $\zeta\text{-Fe}_2\text{N}$  phase, indicated by the doublet seen in Figure 8c. Figure 8d shows the result of exposure of this catalyst to 3/1  $\text{H}_2/\text{CO}$  at  $250^\circ\text{C}$  for 20 hours. This spectrum has the same general appearance of other bulk nitrified samples following FTS and indicates a complex mixture of nitride, carbide and carbonitride phases. Rereduction of this sample resulted in the spectrum shown in Figure 8e, showing major contributions (84%) from a bulk Fe metal pattern. Thus, the iron crystallites have sintered during the nitriding-reaction-reduction process. In previous experiments, we have shown that small particle  $\text{Fe}_4\text{N}$  on carbon has stable activity during Fischer-Tropsch synthesis. Our results here suggest that maintaining the small size of the particles is important to maintaining the stability of the nitride catalyst. The point in the process at which particle growth occurs is currently under investigation.

#### REFERENCES

1. Amelse, J.A., Butt, J.B. and Schwartz, L.H., *J. Phys. Chem.*, **82** (5), 558 (1978).
2. Anderson, R.B. and Hofer, L.J.E., in *Catalysis, Vol IV.* (Emmett, P.H., ed.), Reinhold, New York (1956).
3. Anderson, R.B., *The Fischer-Tropsch Synthesis* Academic Press, Orlando (1984).
4. Niemantsverdriet, J.W., van der Kraan, A.M., van Dijk, W.L. and van der Baan, J. *Phys. Chem.*, **84**, 3863 (1980).
5. Ott, G.L., Fleisch, T. and Delgass, W.N. *J. Cat.*, **65**, 253 (1980).
6. Anderson, R.B., *Cat. Rev.-Sci. Eng.*, **21** 53 (1980).
7. Borghard, W.G. and Bennett, C.O., *ISEC Prod. Res. & Dev.*, **18** 18 (1979).
8. Yeh, E.B., Jaggi, N.K., Butt, J.B., and Schwartz, L.H., *J. Catal.* **91**, 231 (1985).
9. Yeh, E.B., Schwartz, L.H., and Butt, J.B., *J. Catal.* **91**, 241 (1985).
10. Jack, K.H., *Acta Crystallogr.*, **5**, 404 (1952).
11. Grunze, M., Bozso, F., Ertl, G. and Weiss, M., *Appl. Surf. Sci.*, **1**, 241 (1978).
12. Ertl, G., Huber, M., and Thiele, N., *Z. Naturforsch. A.*, **34**, 30 (1979).
13. Shirane, G., Takei, W.J. and Ruby, S.L., *Phys. Rev.*, **126** (1), 49 (1962).
14. Bainbridge, J., Channing, D.A., Whitler, W.H., and Pendelburg, R.E., *J. Phys. Chem. Solid*, **34**, 1579 (1973).
15. Chen, G.M., Jaggi, N.K., Butt, J.B., Yeh, E.B. and Schwartz, L.H., *J. Phys. Chem.*, **87**, 5326 (1983).

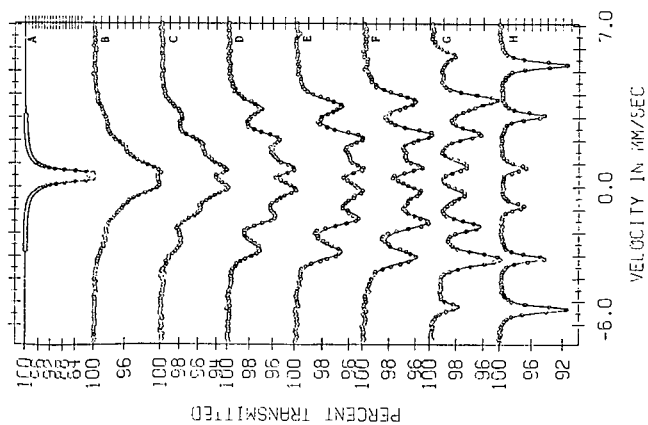


Figure 1. - Room Temperature Mössbauer spectra of iron nitrides.  
 A)  $\gamma$ - $\text{Fe}_3\text{N}$ ; B-F)  $\alpha$ -Fe prepared by exposure of  $\alpha$ -Fe to 9%  $\text{NH}_3$ , 9%  $\text{H}_2$  at 400°C (B), 235°C (C), 280°C (D), 250°C (E) and to 89%  $\text{NH}_3$ , 11%  $\text{H}_2$  at 400°C (F); G)  $\gamma'$ - $\text{Fe}_3\text{N}$ ; H)  $\alpha$ -Fe

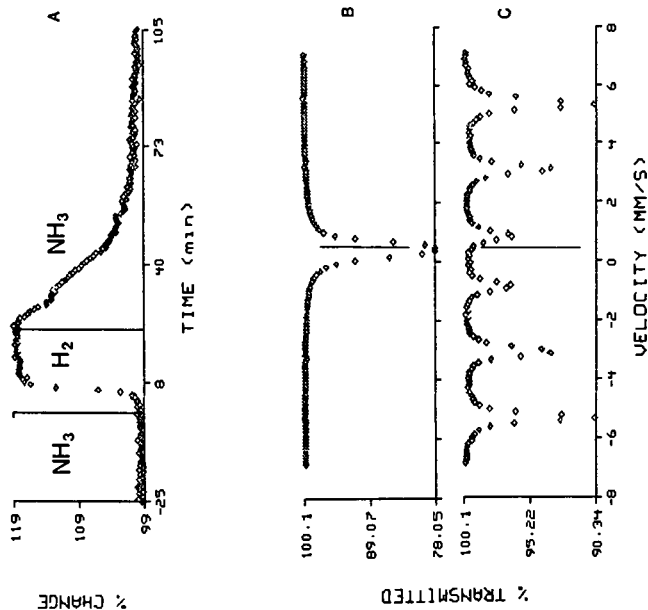


Figure 2. - Mössbauer spectra of  $\gamma$ - $\text{Fe}_2\text{N}$  during nitriding and denitriding.  
 A) Constant velocity spectrum, at the velocity indicated by the lines in spectra B) and C), taken at 325°C during a switch from  $\text{NH}_3$  to  $\text{H}_2$  and back to  $\text{NH}_3$ . B) Spectra of the initial and final  $\gamma$ - $\text{Fe}_2\text{N}$  at 25°C. C) 25°C spectrum of  $\alpha$ -Fe after denitriding.

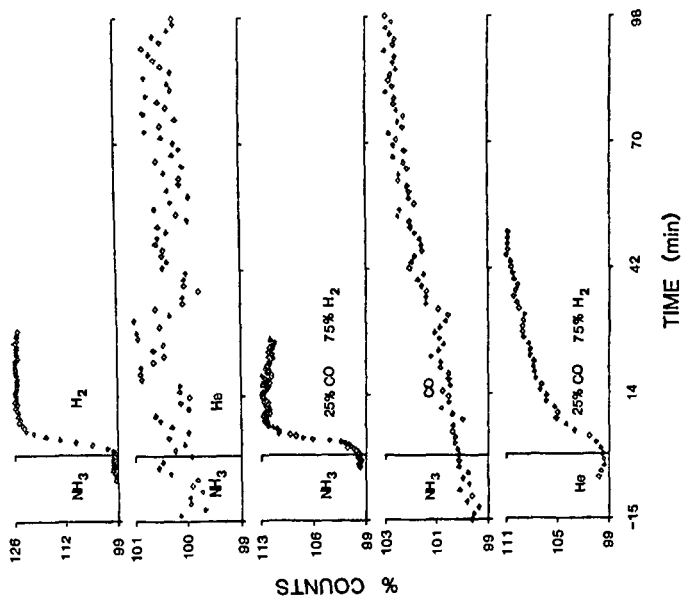


Figure 3. - *In situ* analysis of  $\zeta$ -Fe<sub>2</sub>N stability at 250°C.

- step change to H<sub>2</sub> from NH<sub>3</sub>
- step change to He from NH<sub>3</sub>
- step change to 3H<sub>2</sub>/CO from NH<sub>3</sub>
- step change to CO from NH<sub>3</sub>
- step change to 3H<sub>2</sub>/CO from NH<sub>3</sub> over pre-oxidized  $\zeta$ -Fe<sub>2</sub>N

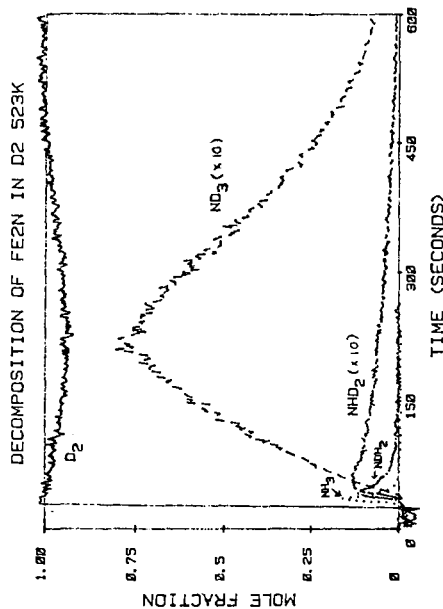


Figure 4. - Decomposition of  $\zeta$ -Fe<sub>2</sub>N in deuterium at 250°C after purging in argon.

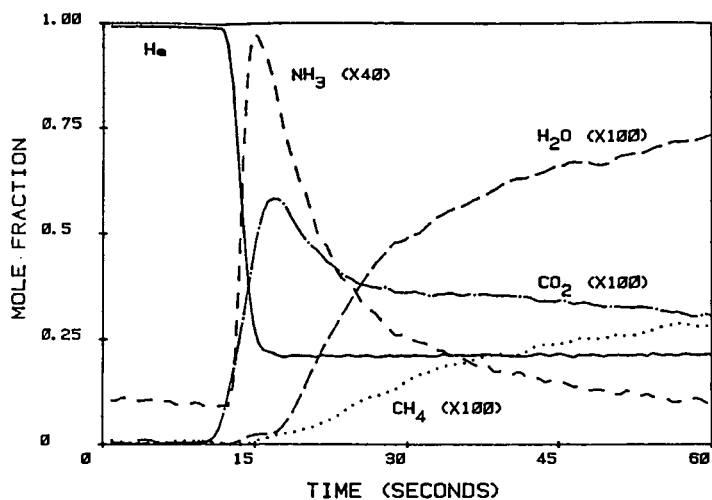


Figure 5. - Step change from helium to 3 H<sub>2</sub>/1 CO/1 He over an  $\epsilon$  nitride at 250°C.

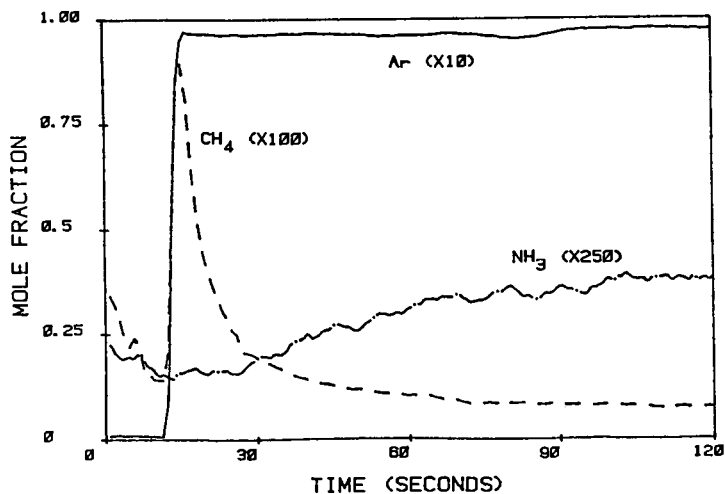


Figure 6. - Step from helium to 10 H<sub>2</sub>/Ar over an  $\epsilon$  nitride after 5 min. of FT synthesis in 3/1 H<sub>2</sub>/CO at 250°C.

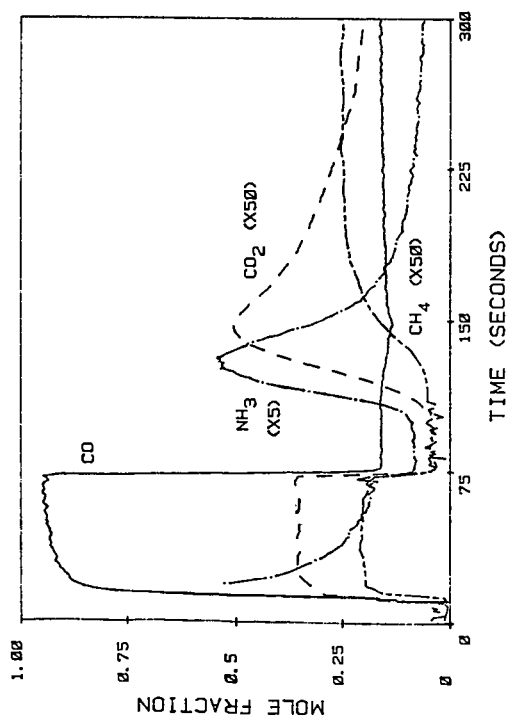


Figure 7. - Pretreatment of a  $\gamma$ -Fe<sub>2</sub>N catalyst in 1 min. of CO followed by 3/1 H<sub>2</sub>/CO at 250°C.

# MOSSBAUER SPECTRA 5Wt% IRON ON CARBOLAC

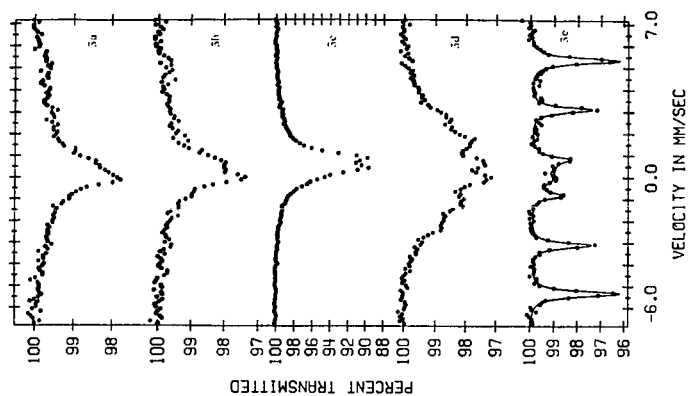


Figure 8. - Mössbauer spectra of 4.5 wt% Fe supported on carbolac.

- a) Reduced in H<sub>2</sub> at 400°C for 16 hrs.
- b) Exposed to He at RT for 21 hrs.
- c) Nitrided to  $\gamma$ -Fe<sub>2</sub>N using 100 NH<sub>3</sub> at 400°C for 8 hrs.
- d) Post - FTS at 250°C for 20 hrs.
- e) Reduced in H<sub>2</sub> at 400°C for 4 hrs.